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Contents

	Page
The Alkaloids of <i>Lycopodium</i> Species. IV. <i>Lycopodium tristachyum</i> Pursh—L. Marion and R. H. F. Manske - - -	1
The Temperature Coefficient of the Diffusion Constant of Copper in Aqueous Solutions of Sulphuric Acid Containing Copper Sulphate—W. A. Patterson and J. T. Burt-Gerrans -	5
Sedimentation Volumes and Rigidity in Suspensions of Sodium Soaps in Mineral Oils— W. Gallay and I. E. Puddington - -	16

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NUMBER 1

THE ALKALOIDS OF *LYCOPODIUM* SPECIES

IV. *LYCOPODIUM TRISTACHYUM* PURSH¹

BY LÉO MARION² AND RICHARD H. F. MANSKE²

Abstract

Besides a small quantity of nicotine, four alkaloids have been isolated from *Lycopodium tristachyum* Pursh. One of these, lycopodine, has been described previously. The remaining three bases appear to be new. They are alkaloid L13 ($C_{16}H_{25}ON$) also found in *L. obscurum*, alkaloid L14 ($C_{16}H_{25}N$), and alkaloid L15 ($C_{20}H_{31}O_4N$).

The authors have embarked upon a series of researches on the alkaloids of *Lycopodium* species the object of which is to isolate the alkaloids present and determine their constitutions in so far as this is permitted by their availability. In addition to the main problem, it is already evident that some taxonomic problems can also be solved. If it be assumed that similarity of alkaloid constituents in plants is indicative of botanical similarities, the converse must be accepted. Plants which are morphologically similar may, however, elaborate different alkaloids and this is taken to mean that they are at least specifically distinct.

Lycopodium flabelliforme Fernald has already been examined (1), but at the time that the paper was written the Linnaean interpretation as *L. complanatum* was accepted. The modern conception is that the species should be subdivided into a number of species. The plant which is the subject of this communication, *L. tristachyum* Pursh, is closely related morphologically to *L. flabelliforme* Fernald but the alkaloids it contains do not reflect such a close relation. Of the more than 10 alkaloids present in both plants only two are common constituents, namely, nicotine and lycopodine. The former is common in Canadian *Lycopodiums* and the latter is present in all species examined by the authors and is present in European species or varieties as well. *L. tristachyum* contains in addition three alkaloids not hitherto described. One of these, alkaloid L13 ($C_{16}H_{25}ON$), is identical with a base isolated from *L. obscurum* L., a plant under investigation. The remaining two alkaloids, L14 and L15, are tentatively assigned the formulae $C_{16}H_{25}N$ and $C_{20}H_{31}O_4N$ respectively.

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² Chemist.

It may be pointed out that with two exceptions all the alkaloids encountered by the authors are either C_{16} or C_{18} bases. The exceptions are alkaloid L15 and a base isolated from a mixture designated as alkaloid L9 (2). Both seem to be C_{20} alkaloids. While there are no a priori reasons to assume that C_{20} bases should not be elaborated by Lycopodiums, their rare occurrence does not inspire confidence in their given formulae. The three new alkaloids together were present to the extent of less than 0.01%.

It is to be added that the plants were identified by Mr. C. A. Weatherby, of the Gray Herbarium, Harvard University, and by Dr. Jacques Rousseau of the Jardin Botanique of Montreal who were consulted independently, and the present opportunity is taken to express grateful thanks.

Experimental

Lycopodium tristachyum Pursh was collected in July and August in open woods on the Quebec side of the Ottawa River, some fifty miles upstream from Ottawa. It was kindly identified by Mr. C. A. Weatherby. A total of 15.7 kg. of dried and ground material was available. It was worked up in the manner already described except that chloroform was used to extract the bases referred to as "crude alkaloid" (1).

Lycopodine

The crude alkaloid was redissolved in dilute hydrochloric acid, the solution filtered through charcoal and extracted with ether until nothing further was removed. The aqueous solution was basified with ammonia and exhausted with ether. This ether solution was dried over pellets of sodium hydroxide and the solvent distilled off. There remained a partly crystalline residue which was dissolved in acetone containing a little methanol and the solution cautiously neutralized with 60% perchloric acid. The crystalline perchlorate which separated was filtered, washed with acetone, and recrystallized repeatedly from boiling water. It melted at $279^{\circ}\text{C}.$ * either alone or in admixture with a specimen of lycopodine perchlorate (m.p. 283°), wt. 27.3 gm. The free base was regenerated and recrystallized from a mixture of absolute ether and hexane. It melted at 116° either alone or admixed with lycopodine.

Nicotine

The acetone mother liquor from the lycopodine perchlorate was diluted with water and evaporated until the organic solvent was largely removed. The remaining aqueous solution, on cooling, deposited a further small crop of lycopodine perchlorate, which was filtered off. The filtrate was basified with ammonia and the precipitated base extracted with large portions of ether. The combined extract was dried over sodium chloride and the solvent distilled off. The residual basic oil was fractionated *in vacuo*. It yielded the following

* All melting points are corrected.

fractions: I, b.p. 80 to 100° C. (< 1 mm.); II, b.p. 115 to 120° (< 1 mm.); III, b.p. 125 to 140° (< 1 mm.); IV, b.p. 140 to 145° (< 1 mm.); V, b.p. 165 to 185° (< 1 mm.), leaving a small undistilled residue.

Fraction I, when redistilled, was obtained as a colourless oil, b.p. 80 to 90° C. (< 1 mm.). It was dissolved in a little methanol and added to a hot methanolic solution of picric acid. A crystalline picrate separated which melted at 226° either alone or in admixture with nicotine dipicrate.

Alkaloid L13

Both fractions II and III on standing deposited small quantities of lycopodine, which was filtered and washed with a little hexane. The mother liquors were combined and evaporated to dryness. The residual oil was dissolved in ethyl acetate and the solution neutralized with perchloric acid. A crystalline perchlorate separated which was filtered and washed with a little ethyl acetate. After two recrystallizations from boiling acetone it was obtained as large prisms melting at 274°. The melting point was not depressed by admixture with the perchlorate of an alkaloid isolated from *L. obscurum*. Calc. for $C_{16}H_{25}ON \cdot HClO_4$: C, 55.25; H, 7.48; N, 4.03%. Found: C, 55.42, 55.18; H, 7.58, 7.56; N, 3.94, 3.81%.

Alkaloid L14

The ethyl acetate mother liquor from the above perchlorate was concentrated and allowed to cool. On standing, a crystalline perchlorate separated which was recrystallized once from boiling water and then from a mixture of methanol and ethyl acetate, from which it was obtained as colourless stout prisms melting at 238° C. Calc. for $C_{16}H_{25}N \cdot HClO_4$: C, 57.93; H, 7.84; N, 4.22%. Found: C, 57.55, 57.72; H, 7.87, 7.99; N, 4.30, 4.29%.

Alkaloid L15

Fractions IV and V were worked up together. The combined base from these two fractions was dissolved in ethyl acetate and the solution neutralized with perchloric acid. The crystalline salt which separated was filtered and washed with a little ethyl acetate. It melted at 276° C. It was suspended in ether and shaken with ammonia. The base was extracted with ether, the solution evaporated on the steam-bath, and the residue distilled *in vacuo*. The distillate crystallized immediately and, after recrystallization from hexane, melted at 117° either alone or in admixture with lycopodine.

The combined ethyl acetate filtrate and washings was poured into water and heated on the steam-bath until all the organic solvent had evaporated. The resulting concentrated aqueous solution was allowed to cool slowly. A crystalline perchlorate gradually separated which was filtered and washed with a little water. After two recrystallizations from methanol-ethyl-acetate, from which it separated as small prisms, it melted at 231° C. Calc.

for $C_{20}H_{31}O_4N \cdot HClO_4$: C, 53.39; H, 7.12; N, 3.12%. Found: C, 53.78, 53.89; H, 7.17, 7.30; N, 2.90, 2.96%.

The mother liquors from the various fractions were all worked up until neither free bases nor perchlorates could be crystallized. There was thus left only a small quantity of resinous products.

The small undistilled residue left from the fractionation of the bases was taken through acid and converted to perchlorate, but it failed to yield any crystalline salt.

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1. MANSKE, R. H. F. and MARION, L. Can. J. Research, B, 20 : 87-92. 1942.
2. MANSKE, R. H. F. and MARION, L. Can. J. Research, B, 21 : 92-96. 1943.

THE TEMPERATURE COEFFICIENT OF THE DIFFUSION CONSTANT OF COPPER IN AQUEOUS SOLUTIONS OF SULPHURIC ACID CONTAINING COPPER SULPHATE¹

BY W. A. PATTERSON² AND J. T. BURT-GERRANS³

Abstract

This paper presents values of the temperature coefficient of the diffusion constant of copper in aqueous solutions of sulphuric acid containing copper sulphate, for the range 10° to 25° C. and four acid concentrations. The work is based on the Mathematical Theory of the Changes of Concentration at the Electrode, formulated by Rosebrugh and Miller. Evidence is presented supporting the choice of a new point on the oscillograph potential curve for the measurement of t . The values of K , thus obtained, at 18° C. are in agreement with those of Cole and Gordon, who used the method of Northrop and Anson. The values of K at 10° C. calculated from those at 25° C. by means of viscosity data are in agreement with the values obtained by experiment.

Nomenclature

- A = Area of electrode,
- $a = \frac{\pi^2 K}{4l^2}$,
- $C = G/K$,
- $G = \frac{I}{96540 A}$,
- g = grams of copper per litre of solution,
- I = current, amp.,
- I' = limiting current,
- K = diffusion constant,
- l = thickness of the diffusion layer,
- $m = 2n - 1$,
- n = an integer,
- t = time required (seconds) for concentration potential to reach a maximum,
- t' = time interval of curve $C-D$,
- u = mobility of ion,
- x = distance normal to the electrode,
- z = equivalents of copper per cubic centimetre of solution at time t ,
- z_0 = initial concentration of copper,
- z' = final concentration of copper at electrode, after electrolysis.

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Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont. A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Toronto.

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Introduction

The Rosebrugh and Miller (9) mathematical theory of changes of concentration at the electrode brought about by diffusion and chemical reaction has been experimentally proved by Redman (8), Burt-Gerrans (1), and Gordon (4) for maximum conducting sulphuric acid solutions of copper sulphate at 18° C.

From the expressions developed by Rosebrugh and Miller, the diffusion constant K and the thickness l of the diffusion layer may be calculated if I' , the limiting current (i.e., that current which in infinite time is just sufficient to bring the concentration z at the electrode from z_0 , the initial concentration, to some known concentration, z'), and t , the time needed to bring about the same change in concentration by another current I greater than the limiting current, have been determined.

Burt-Gerrans obtained the value of $4.0 \pm 0.1 \times 10^{-6}$ for K , for copper in 7.6 N sulphuric acid solutions of copper sulphate, at 18° C. This does not check with the value obtained by Cole and Gordon (2), who used the method of Northrop and Anson (7). The present paper proposes to show reasons for this discrepancy and also to present values of K for the range 10° to 25° C. for four concentrations of sulphuric acid.

The Apparatus

The apparatus used is essentially that designed by Burt-Gerrans (1). Certain mechanical modifications have been added but an adequate description is not necessary for the present paper. However, a review of the essential apparatus and functions of the electrical circuits is included.

In essence, it consists of a two-element Siemens-Blondell oscillograph, a copper cell, and associated electrical circuits. The cell is provided with three copper cathodes on the same rotating shaft, insulated from one another by thin strips of Redmanol. The three cathodes are of the same diameter (4.475 cm.) and height (5.72 cm.). The common anode, which also acts as the cell, is a drawn copper cylinder 10.2 cm. internal diameter and 21 cm. high.

The electrical circuits were designed:—

1. To send and to measure a current of electricity through each section of the three section rotating copper cathode.
2. To register on an oscillogram the potential drop between the centre section of the cathode and the anode during the first fraction of a second of the electrolysis.
3. To register simultaneously on the same oscillogram a timing wave, with which to measure the duration of electrolysis and the time of potential change accompanying it.
4. To measure the speed of rotation of the cathode by short circuiting the timing wave, once for every revolution of the cathode.

5. To place zero voltage and calibration voltage lines on the oscillogram prior to any electrolysis.

6. To place a calibration line for measuring any change of current through the cell, the change being registered by a deflection of the timing wave on the oscillogram.

The above are the main circuits; others include means for measuring the limiting current, etc.

The preparation of the cell for electrolysis was the same as that described by Burt-Gerrans. The cathode was highly polished and the solutions were saturated with carbon dioxide to prevent solution of the copper. Electrolytic polishing of the cathode was tried for a time, but the results did not appear to be any better than those obtained from mechanical polishing. The copper analysis was done electrolytically.

Equations and Calculations

The two chief equations from the Rosebrugh and Miller theory are:—

For $x = l$

$$\frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2} \sum \frac{1}{m^2} e^{-m^2 at}, \quad (16 R \text{ and } M)$$

where $C = G/K$, $G = \frac{I}{96540 A}$, A being the area of the electrode;

$m = 2n - 1$, n being an integer; $at = \frac{\pi^2 K t}{4l^2}$ and

[for $t = \infty$, $x = l$]

$$I' = \frac{96540 KA (z' - z_0)}{l(1 + z\mu/\sum z\mu)}. \quad (24 R \text{ and } M)$$

There are two methods of calculation, starting with Equation (16 *R* and *M*), depending on whether the electrolysis current I is greater or less than twice the limiting current I' . These are respectively the parabolic approximation and the first term approximation.

The parabolic approximation has been used in this work because its final form is simpler than that of the first term approximation and does not require nearly as accurate limiting current measurements as is required with the first term approximation, since the value of I' enters directly into the latter.

Therefore, if $I > 2I'$, Equation (16 *R* and *M*) reduces to

$$\frac{z - z_0}{Cl} = \frac{4}{\pi^{3/2}} \sqrt{at} \text{ (approx.)}. \quad (22a R \text{ and } M)$$

By substituting I'/I for $\frac{z - z_0}{Cl}$ and $\frac{\pi^2 K t}{4l^2}$ for at , (22a) becomes

$$I'/I = \frac{4}{\pi^{3/2}} \sqrt{\frac{\pi^2 K t}{4l^2}}.$$

This is equated with (24 R and M), and, since $z' = 0$ from our limiting current measurements and $\frac{z\mu}{\Sigma z\mu}$ is approximately zero for a solution of copper sulphate in concentrated sulphuric acid, and if the value of 80.5 sq. cm. for A is substituted, the final equation for K is

$$K = \frac{2.119 \times 10^{-6} I^2 t}{g^2}, \quad (1)$$

where g = grams of copper per litre of solution.

The Measurement of t and the First Experimental Results

Fig. 1 shows a typical polarization curve as recorded by the oscillograph. The point of inflection D was taken by all previous investigators for the measurement of t , it being given by a timing curve (not shown) of 128 waves per sec.

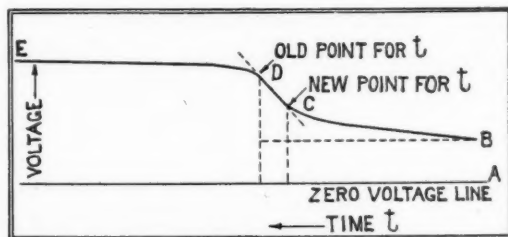


FIG. 1.

Using the point D , the present investigators obtained values of K for 30.75% and 15.36% sulphuric acid concentrations, at 10°, 15°, 20°, and 25° C. The copper concentrations in this and all subsequent experiments ranged from 1 to 4 gm. per litre. The average values for 12 to 20 determinations are plotted in Fig. 2, and the experimental data for one temperature and acid concentration are given in Table I.

Fig. 2 also includes the average value of K (about 40 determinations under various conditions), 4.04×10^{-6} , for maximum conducting acid, at 18° C. obtained by Burt-Gerrans and one determination obtained by Gordon for a solution of the same concentration at 30° C. but saturated with air instead of carbon dioxide.

The numbers are in good agreement with, and thus confirm, the results of earlier workers with this apparatus. But they are not in agreement with values of K obtained by Cole and Gordon (2), using the method of Northrop and Anson (7). At 18° C. for the range of copper concentrations* used by us and for 30.46 and 15.91% sulphuric acid concentrations, Cole and Gordon's values are 3.55×10^{-6} and 4.85×10^{-6} respectively. Our results are $4.07 \times$

* Rosebrugh and Miller postulated that K did not change with concentration of solute. Since our range of concentrations, 1 to 4 gm. of copper per litre, is very small this can be accepted for our conditions.

TABLE I
TEMP., 25° C. 30.75% ACID

Osc. No.	Gm. cu. per litre	<i>t</i> , sec.	<i>I</i> , amp.	Sec. per rev.*	<i>K</i> × 10 ⁶
9B	1.906	0.1544	2.329	0.122	4.89
9C	1.906	.1360	2.453	.118	4.77
9D	1.906	.0903	2.997	.120	4.73
9E	1.906	.0820	3.147	—	4.74
20A	4.182	.2342	4.059	.086	4.68
20B	4.182	.2295	4.088	.082	4.65
20C	4.182	.2235	4.142	.080	4.65
20D	4.182	.2175	4.225	.082	4.70
20E	4.182	.1922	4.438	.082	4.59
23B	1.710	.3155	1.437	.125	4.72
23C	1.710	.2815	1.531	.124	4.78
23D	1.710	.2350	1.659	.123	4.69
23E	1.710	.2090	1.769	.111	4.74
24B	2.019	.1592	2.424	.118	4.86
24C	2.019	.1445	2.527	.117	4.80
24D	2.019	.1355	2.596	.117	4.75
24E	2.019	.1250	2.700	.115	4.74
					Av. 4.73

* While the speeds of rotation of the cathode do not enter into the calculations here, they are inserted so that the cathode conditions may be more fully understood.

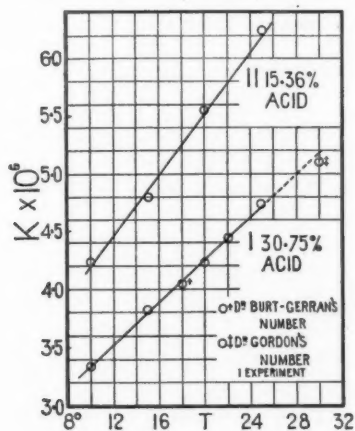


FIG. 2.

10^{-6} and 5.25×10^{-6} for 30.75 and 15.36% acid concentrations respectively. The values of K of Cole and Gordon have been corrected for a 3% error in a calibration factor as noted by Gordon (5).

The Investigation of t

This discrepancy increased our interest in the reliability of our measurement of t . As indicated by the records of previous workers, the use of the point D was purely arbitrary. The potential curve was analysed as follows (Fig. 1): $A-B$, the IR drop plus an instantaneous overvoltage, present on all curves; $B-C-D$, the concentration potential; $D-E$, the hydrogen overvoltage. Since $D-C$ is only about 0.25 volts for the above curve, it is evident that such an analysis indicates a rather low hydrogen overvoltage.

Further, the $B-C$ curve has one form, while $C-D$ is, as closely as can be measured, a straight line. It therefore appeared justifiable to take C , where the transition from one type of curve to another occurs, as the point where there is a discontinuity in the cell reaction. Since $C-D$ was almost invariably a straight line (exceptions noted later), the new point could be obtained readily by drawing a straight line down beside the steep incline.

This straight line part of the curve supported the view that most of the upper part of the curve is a hydrogen overvoltage. It has been shown, with mercury electrodes (3, p. 489) and with platinum electrodes (6, p. 455) that the rise of hydrogen overvoltage is a linear function of time, up to the point where it tends to level off, the flattening being associated with the gross evolution of gaseous hydrogen, the duration of linearity being 0.1 and 0.01 sec. respectively. The corresponding times in our curves were 0.02 to 0.03 sec.

Using the new point, values of t for all oscillograms were redetermined. Fig. 3 shows the new average values of K with those of the old method for comparison. Table II compares them with those of Cole and Gordon.

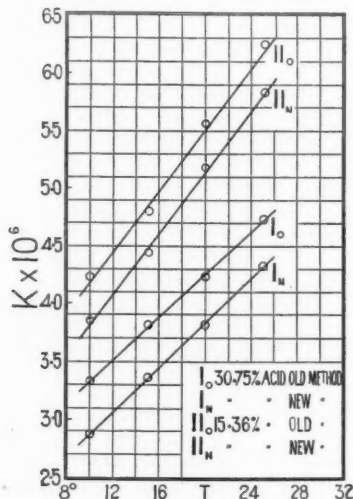


FIG. 3.

TABLE II

K , Old method	K , New method	Acid conc. %	K , Cole's	Acid conc. %
4.07×10^{-6}	3.63×10^{-6}	30.75	3.55×10^{-6}	30.46
5.25×10^{-6}	4.88×10^{-6}	15.36	4.85×10^{-6}	15.91

There seems little doubt that these results check those of Cole and Gordon.

Certain Properties of $C-D$

In Fig. 3 the new curves are, within experimental error, parallel to the old. It can be shown from Equation (1) that this is true if $\partial t' / \partial T = 0$, where t' is the time corresponding to $C-D$. Obviously this part of the curve is not part of the concentration potential and should not enter into the calculations for K . The slight deviation from parallelism of the 30.75% acid curves indicates, if anything, a negative $\partial t' / \partial T$, whereas it would have had to be positive for the concentration potential. Its magnitude is also too small to be significant.

If $C-D$ be not due to copper, then a similar curve should be obtained from acid solutions containing no copper. Fig. 4 shows the curves obtained from

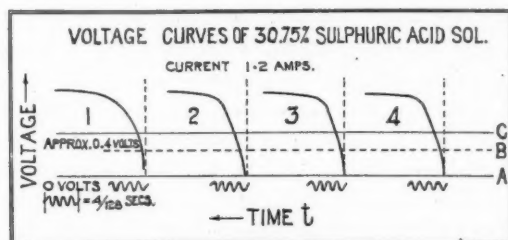


FIG. 4.

four consecutive electrolyses of a solution of maximum conducting sulphuric acid. Similar curves were obtained for 15% acid. $A-B$ here again is the IR drop plus an instantaneous overvoltage, and C , a calibration line. The linearity of the last three curves is apparent but is absent in No. 1. This latter condition was exhibited (by copper sulphate solutions) by many first electrolyses of a series on the same solution. Also the first electrolysis, especially after the electrode had been used as an anode, as in electrolytic polishing, yielded a curve as in Fig. 5. This anomalous behaviour of cathodes after having been used as anodes is characteristic of the measurements of hydrogen overvoltage. Evidently the appearance of the curves is due to some surface condition of the electrode which disappears with successive electrolyses.

The fact that both these phenomena occurred in solutions without copper sulphate again suggests that this part of the P. D. curve is not part of the concentration potential.

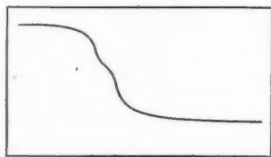


FIG. 5.

The above phenomena had a marked effect on the values of K , calculated by the old method. In a great many cases, the first electrolysis gave a value for K which was so much higher than those obtained from the succeeding electrolyses that these particular values were omitted when calculating the averages. It should be mentioned that all previous investigators noted similar results.

The new method, however, by eliminating this part of the curve, brought all these initial curves into agreement with the rest. No fewer than 12 such curves were thus corrected.

Curve $B-C$, Fig. 1, represents a potential drop of 0.31 v., as obtained from the average of all curves for acid concentrations from 2.0 to 30.75%. The mean deviation was 0.016 v., hardly more than the measuring error. It was also shown that the P.D. was very slightly greater for the higher copper concentrations. The constancy of the above potential drop is what might be expected if $B-C$ is the concentration potential alone. It is in great contrast to the potential variation of the curve $C-D$. Here the polarization changes from 0.35 v. to 0.24 v. with concentrations of 2% to 30.75% acid. The average results are plotted in Fig. 6. Our conceptions of concentration potentials would need revision if these potentials varied in this manner with acid concentration. On the other hand, hydrogen overvoltages do appear to behave this way, although definite confirmation in the literature has not been found.

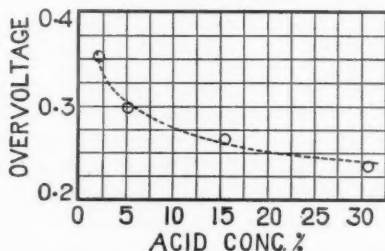


FIG. 6.

Survey of the Evidence

To sum up, we consider that the new method for obtaining t gives a truer value of t as required for the formulae of Rosebrugh and Miller, for the following reasons:

1. The time interval of $C-D$ is independent of temperature, whereas the time interval for the concentration voltage curve required for the measurement of K must be dependent on temperature.
2. $C-D$ shows definite characteristics of a hydrogen overvoltage since,
 - (a) It is a linear function of time,
 - (b) It varies with the acid concentration, the higher the acid concentration the lower the overvoltage.
3. Voltage curves obtained with no copper in solution showed characteristics similar to $C-D$.
4. The value of K calculated from all initial electrolyses of a series on the same solution were brought into excellent agreement with the rest of the numbers.
5. Values of K at 18° C. calculated from the new values of t using other temperatures and the temperature coefficient, are in the same range as those of Cole and Gordon.

Further Experimental Results

Experiments were continued using 5.09 and 2.03% sulphuric acid solutions. The former gave a linear temperature curve but the results for 2.09% are anomalous in that at 10° and 25° C. values of K from different copper concentrations could not be averaged. Moreover the curves for single copper concentrations were concave. The average values of K are plotted in Fig. 7 according to the data given in Table III.

TABLE III
2.03% SULPHURIC ACID

Cu., gm. per litre	10° C.	15° C.	20° C.	25° C.
Approx. 1.3 gm.	4.95×10^{-6}	5.59×10^{-6}	6.48×10^{-6}	7.53×10^{-6}
From 2.1 to 2.6 gm.	4.75×10^{-6}	5.54×10^{-6}	6.50×10^{-6}	7.79×10^{-6}

Fig. 7 shows the diffusion constants plotted against the acid concentration for five temperatures as taken from our temperature coefficient curves. The results of Cole and Gordon are also plotted. The agreement for 5.09 and 2.03% acid continued to be good.

An explanation for the behaviour of 2.03% acid solutions has not been found. It appears to be no longer safe to assume that K is independent of concentration. Migration effects also possibly enter the picture.

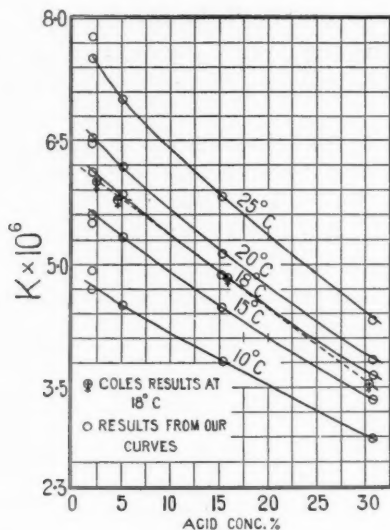


FIG. 7

Discussion of Results

The mean percentage deviation of individual values of K varied from 1.35% for 30.75% sulphuric acid to 0.93 for 5.09%. This decrease is almost entirely due to the accuracy in measuring t . The consistent measurement of t depends to some extent on the operator in that he may reduce his deviation in the measurement of t from about 2% to less than 1%, depending on how his technique improves with time.

Comparing the method of Northrop and Anson with ours, we note that the electrolytic method is much faster for individual measurements and does not require calibrating solutions. The former method, however, does not require apparatus so intricate, is much cheaper, and is less restricted in its use.

The importance of the present work lies in the fact that by two totally different methods, diffusion constants have been obtained which are in agreement, and this furnishes a verification of both methods as well as of the validity of the mathematical theory of Rosebrugh and Miller. It should be pointed out that Cole's values of K are differential, whereas ours are integral, but owing to the low concentrations and small range used by us, they may also be considered as differential diffusion constants.

Viscosity Relationships

For uncharged particles the Stoke's-Einstein equation for diffusion is:—

$$K = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r},$$

where R is the gas constant; T , the absolute temperature; N , Avogadro's number; r , the radius of the diffusing particle, and η , the coefficient of viscosity of the diffusing medium. Assuming r constant for any one acid concentration, it was shown that our diffusion constants are consistent with such an equation as this, in that the diffusion constant for one temperature could be calculated from that at another temperature, if the viscosity coefficients were known for both temperatures.

Table IV shows such a calculation for values of K at 10°C . from those at 25°C . The diffusion data are taken from Fig. 7. The viscosity data required were taken from the I.C.T., supplemented by our own measurements. The observed and calculated values of K are in excellent agreement. Similar results were obtained for 15° and 20°C .

TABLE IV
 $K_{10^\circ\text{C}}$ FROM $K_{25^\circ\text{C}}$ BY VISCOSITY CALCULATIONS

Acid, %	$K_{25^\circ\text{C}}$	$K_{10^\circ\text{C}}$, Calc.	$K_{10^\circ\text{C}}$, Obs.
30.0	4.42×10^{-6}	2.84×10^{-6}	2.92×10^{-6}
25.0	4.90	3.18	3.23
20.0	5.37	3.53	3.53
15.0	5.87	3.82	3.84
10.0	6.41	4.12	4.16
5.0	7.03	4.52	4.51

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SEDIMENTATION VOLUMES AND RIGIDITY IN SUSPENSIONS OF SODIUM SOAPS IN MINERAL OILS¹

BY WILFRED GALLAY² AND IRA E. PUDDINGTON²

Abstract

The equilibrium sedimentation volumes of sodium soaps in suspension in mineral oils have been measured. The sedimentation volume increases greatly with decrease in viscosity index of the oil. Flow-pressure relations, determined with a torsional viscosimeter, show that suspensions with large sedimentation volumes possess rigidity, whereas the flow is Newtonian in suspensions having small sedimentation volumes. Variation in sedimentation volume is therefore caused by difference in the tendency toward agglomeration or attraction between particles, leading to the formation of branched chains and scaffolding structures, with consequently greater sedimentation volumes.

Sedimentation Volumes of Sodium Soaps in Oils

The volumes occupied by finely powdered solids in various liquids is of general interest, and is of considerable importance in a number of types of industrial products. The general problem has been discussed by the authors elsewhere (1). The special case of the sedimentation of soaps in mineral oils would appear to have a direct bearing on the nature of the interface in such systems, and this has been shown in turn to be a major factor in the physical properties of such dispersions (4).

It is well known that a powdered solid shows different equilibrium settling volumes in various liquids. This variation has been ascribed by Ostwald and Haller (5) to "lyospheres" of different sizes. A lyosphere is defined as a shell of liquid bound to the particle of solid by adsorption forces, and the whole concept on this basis has been termed "lyosorption". These terms describing the hypothetical explanation have been used by other workers. Ostwald and Haller have noted a rough trend of correlation between the dielectric polarization value of the liquid medium and the sedimentation volume in that liquid. An alternative explanation, and one that can be well substantiated by experimental findings, has been advanced by us (1), as follows. The sedimentation volumes are directly dependent on the degree of flocculation of the dispersed particles in the suspension. This flocculation is a result of sticking or attraction between the surfaces of neighbouring particles. Further evidence for this interpretation is given in the present work.

Experiments were carried out to determine the effect of various factors on the equilibrium settling volumes of sodium soaps in mineral oils. The soap, generally 2 gm. in weight and sufficiently fine to pass a 240 mesh sieve, was made up to 50 cc. volume with the oil in a stoppered graduate. After thorough

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shaking, the suspensions were allowed to stand, and the volume occupied by the soap was read at intervals until equilibrium was reached. The suspensions were maintained in thermostats during settling. Table I shows some results obtained with sodium oleate in four different mineral oils at various temperatures.

TABLE I

EQUILIBRIUM SEDIMENTATION VOLUMES OF SODIUM OLEATE AT VARIOUS TEMPERATURES

Temp., °C.	Oil		Sedimentation volume, cc.
	V.I.	Visc. (S.U.S. at 100° F.)	
25	40	900	25.0
	95	900	9.0
	40	100	9.5
	95	100	7.9
80	40	900	39.5
	95	900	12.9
	40	100	18.3
	95	100	14.0
100	40	900	50.0
	95	900	17.0
	40	100	*
	95	100	*

* The suspension showed creaming.

It is noted that the volume occupied by equal quantities of soap increases greatly with an oil of lower V.I. for the same viscosity; this is particularly marked with the higher viscosities. For the same V.I., the sedimentation volume increases with higher viscosities of the oil, as might be expected. The sedimentation volume increases markedly with temperature.

Further results are shown in Table II, in which the volumes are expressed in terms of height of the settled soap in tubes of standard diameter. The data are those recorded after three days sedimentation at room temperature.

In this series also it is noted that the volume occupied by a given amount of soap is greater in the low V.I. oil. With the same oil, the oleate occupies in all cases a greater volume than the stearate. The effect of added free fatty acid is to increase the volumes, in particular those of lower value. Free alkali, on the other hand, decreases the previously greater settling volumes.

The variation in sedimentation volumes obtained in such systems admits of an explanation other than that based on the concept of adsorbed shells of liquid. The tendency toward flocculation of particles is very marked in some suspensions, and it would appear that this has a direct bearing on the volume of sedimentation. If the attraction between particles is slight, then the particles can settle past one another and occupy a relatively small volume at equilibrium. A dense packing is attained, particularly in settled suspensions containing isodimensional particles, and furthermore the resistance to redis-

TABLE II
EQUILIBRIUM SEDIMENTATION VOLUMES IN VARIOUS SOAP-OIL SUSPENSIONS

Soap	Oil	Height of suspension, cm.
Neutral sodium stearate	900 vis., 40 V.I.	3.0
	900 vis., 95 V.I.	1.8
	100 vis., 40 V.I.	1.9
	100 vis., 95 V.I.	1.4
Sodium stearate, 10% F.F.A.	900 vis., 40 V.I.	3.3
	900 vis., 95 V.I.	3.3
	100 vis., 40 V.I.	3.0
	100 vis., 95 V.I.	2.9
Sodium stearate, 2.5% free alkali	900 vis., 40 V.I.	1.8
	900 vis., 95 V.I.	1.9
	100 vis., 40 V.I.	1.9
	100 vis., 95 V.I.	1.9
Neutral sodium oleate	900 vis., 40 V.I.	3.7
	900 vis., 95 V.I.	2.5
	100 vis., 40 V.I.	2.4
	100 vis., 95 V.I.	2.2

persion by shaking is very marked. These properties are particularly evident in systems showing strong dilatancy (2). It is apparent however that a slight degree of sticking between surfaces of neighbouring particles will prevent the settling to a densely packed state. A scaffolding structure will result, and under such conditions, a given weight of powdered solid will occupy a much greater sedimentation volume at equilibrium. This is shown diagrammatically in Fig. 1.

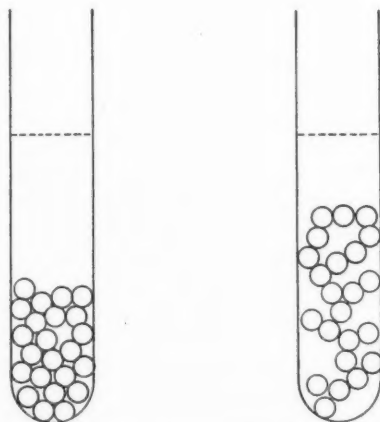


FIG. 1. Diagrammatic representation of increased sedimentation volume due to flocculation.

Viscosity and Rigidity

Suspensions in which the dispersed phase is arranged in connecting branched chains should possess appreciable rigidity of structure. Liquid is held enmeshed within such a structure and is in general incapable of flow, as a result of surface tension forces. If a scaffolding structure is present, an applied force must effect some breakdown in this structure before flow can begin. The stress at which deformation or flow is just initiated is generally termed the yield point. Following the yield point, further increased stresses result in greater flow, and the flow-pressure relation will depend on the properties of the system under investigation.

The property of rigidity in sodium-soap-oil suspensions was investigated with a modified Stormer viscosimeter by means of which the flow could be measured over a wide range of loads. Suspensions of sodium stearate were prepared in 900 vis. 40 V.I. oil and 900 vis. 95 V.I. oil, all in 50% concentration by weight. Measurements were carried out on the freshly prepared suspensions and also after they had stood at room temperature for one week.

The data are shown graphically in Fig. 2, in which the flow is plotted against the applied load. The instrument error was of the order of 3 gm. load. The fresh suspensions show a linear flow-pressure relation and there is no appreci-

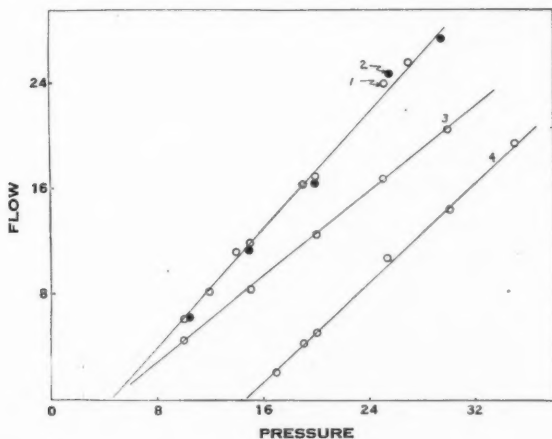


FIG. 2. Flow-pressure relation in sodium stearate suspensions in 900 vis. oils:— 1 and 2, freshly prepared suspensions in 95 V.I. and 40 V.I. oil respectively; 3 and 4, suspensions in 95 and 40 V.I. oil respectively, after standing one week.

able yield value. There is no significant difference in viscosity in the two freshly prepared suspensions. After it has been allowed to stand for a week in order to attain equilibrium, the suspension in the high V.I. oil shows a considerable increase in viscosity, but no yield value has been developed. Small initial stresses bring about a corresponding rate of flow, and there is no

appreciable discontinuity such as would result from the use of this energy in breaking down a preformed structure in the suspension.

In the low V.I. oil the suspension shows a much greater increase in viscosity on standing than in the high V.I. oil. Less free liquid is available for flow, and the mobility slope is greatly decreased. In addition, however, it is apparent that a definite yield value or rigidity has been developed in this suspension. A moderately large force must be exerted in order to break down a pre-existing structure to permit flow to begin, and then a linear flow-pressure relation is obtained. A great deal of evidence has been accumulated (3) to show that such systems possess a true yield value, i.e. the flow-pressure relation remains linear at very small rates of flow and there is no appreciable tendency for a curvature of the viscosity line towards the origin.

The hypothesis that an adsorbed shell of liquid surrounds each particle would involve a gradation of these secondary forces with distance from the surface of the particle. Such a system would show increased viscosity but no rigidity. The present work shows however that the suspension having a large sedimentation volume possesses a structure that must be broken down before flow can begin. Such a structure must be ascribed to a flocculation of particles to form branched chains and a scaffolding structure, which must in turn lead to a greater sedimentation volume as shown in Fig. 1. On the other hand, the suspension showing a relatively small sedimentation volume possesses no appreciable yield value or rigidity, and the flow is Newtonian, like that of a liquid or true solution.

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